EFFECTS OF CRYSTAL ORIENTATION AND TEMPERATURE ON H-IMPLANTATION IN OLIVINE.

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Introduction: Hydrogen (H), the most abundant element in the solar system, plays a crucial role in planetary evolution and also influences biological life activities [1–3]. H+ implantation is an important pathway for incorporating hydrogen into the material of the solar system, as evidenced by the presence of H/OH in the regolith of the airless bodies [4–5]. Despite extensive simulation experiments have been conducted [6–9], several key factors that can significantly affect the implantation process of hydrogen have not been well constrained, including crystal orientation of implanted minerals and radiation temperature. In this study, we conducted the H ions implantation experiments on the olivine with different crystal orientations and temperature conditions and presented the results of analyses of H profile distribution, microstructural changes, and chemical characteristics.

Experimental protocols: Lattice plane selection. Forsterite (Fo90-91) samples were selected and prepared as double-side polished slices with thickness of ~200 μm. Three crystal orientation, including [100], [010], and [001], were determined by Electron Back Scatter Diffraction.

Ion implantation. The H-implantation experiments were performed by using an ion implanter with temperature control system at The State Key Laboratory of Lunar and Planetary Science, Macau University of Science and Technology. H ions beams produced by the ionized pure H2 gas (99.9999 %) in gas ions source was accelerated to an energy of 10 keV. The H+ flux of all implanted samples was controlled at 1.1 ± 0.2 ions/cm² and the flux was ~7.94 × 10¹² ions/cm²·s. For the three orientations experiments, the implanted temperature was set as 25°C. In the temperature-controlled experiments, the crystal orientation was selected as [010] and the implanted temperature was 100°C, 200°C, 300°C and 400°C, respectively. During the irradiation processes, the pressure was controlled at ~2 × 10⁻¹ Torr to simulate the high vacuum conditions of the solar space.

Secondary ion mass spectrometry (SIMS). The depth profiles of implanted H ions were obtained by the Cameca IMS 6f at Arizona State University. A 20 nA O+ ion beam was rastered on a 125 × 125 μm² surface area on each sample. The field aperture set the analyzed area to 750 μm diameter. H+, 16O+, and 30Si+ were measured on an electron multiplier.

Transmission electron microscopy (TEM). We first prepared the electron-transparent microscope foils of the samples using a Dual Beam focused ion beam (FEI Helios G5 UX). High resolution images and crystal diffraction patterns of the foils were obtained with a TEM (FEI TALOS F200X) at Sinoma Institute of Materials Research (SIMR), Guangzhou, China.

Result and Discussion: Orientation effects: TEM images reveal that three crystal orientations of olivine suffered varying degrees of radiative damage and appeared different structural characteristics after H ions implantation (Fig. 1). The radiation damage rim perpendicular to the [100] direction is ~180 nm thick, and amounts of nano-scaled vesicles are produced in the amorphous area. The thickness of damage rim of [010] sample is thicker than that of [100], about 220 nm. Furthermore, the [010] sample has almost no vesicles development but some nanocracks occur in amorphous area. Both vesicles and nanocracks are produced in the radiative damage area (~200 nm thick) of [001] sample. The SIMS data elucidate the similar H/Si profile trends for all three orientations, revealing an initial decrease, followed by stabilization at a saturation plateau, and
ultimately a descent to baseline levels. However, there are differences in some details: (1) Prior to the plateau, the H/Si for the [100] sample decreases more gradually than the other two, with the shortest extension of the plateau and the most rapid return to baseline. (2) The plateau of H/Si for [010] sample is the lowest, and its subsequent rate of decline is slowest. (3) The H/Si profile of the [001] sample displays a rate of variation that is intermediate between the other two orientations.

Overall, the structure damage of olivine corresponds to the distribution of implanted H as indicated by the depth profile. The descent from the highest surface value to the plateau reflects the concentration change of implanted H in the completely amorphous rim. And the saturation plateau signifies the maximum value of H that partially amorphous olivine (retaining some crystallinity) can accommodate. The decline of H/Si beyond the platform is related to the maximum penetration depth of the implanted H and its subsequent diffusion. Comparing the results of three orientations samples, the H ions implantation along direction [100] is the most difficultly to destroy the olivine crystal structure, resulting in the implanted H concentrating near the surface, which promotes the formation of vesicles. Simultaneously, these vesicles provide more vacancies for implanted H to occupy, corresponding to the highest H content observed prior to the saturation plateau among three orientation in the SIMS data. On the contrary, the implanted H can easily penetrate olivine along the orientation [010] and mainly remains in the interlayer cavity that grow up to the nanocracks finally. This accounts for the [010] sample having the most extended saturation plateau in the H/Si depth profile compared to the other two directions. As for the [001] orientation, both the damage imparted by the implantation and the hydrogen distribution are intermediate between that of the [100] and [010] orientations.

**Temperature effects:** Compared to the condition at 25°C, the olivine samples subjected to H ions implantation at 200°C exhibit wider nanocracks and a pronounced formation of vesicular structures in the amorphous area (Fig. 2A). As the implantation temperature rises to 400°C, the cracks further enlarge to ~460 nm in length (Fig. 2B). Despite these microstructural transformations, the depth of radiation damage remains consistent, ranging from 220 to 240 nm. SIMS data reveal that an inclination for the H/Si ratio to increase within the depth profile as the implantation temperature escalates from 25°C to 200°C (Fig. 2C). However, upon surpassing the 200°C, there is almost no change in the H/Si profile trend (Fig. 2D). These findings imply that elevated radiation temperatures precipitate microstructural alterations in the damaged region and an expansion in vacancy sites, which potentially enhances both the saturation value and hydrogen retention capabilities. Nonetheless, once implantation temperatures exceed 200°C, even with the enlargement of nanocracks, hydrogen storage appears to hit a plateau, which could be intrinsically linked to the mineral’s properties and the initial kinetic energy of H ions beam [8, 9].

Fig. 2 (A-B) TEM imaging of olivine implanted with H ions along [010] orientation at 200 °C and 400°C; (C-D) Depth profiles of H/Si under various temperature settings.

In summary, our experiment results indicate that both the crystal orientation and implantation temperature can significantly impact the distribution of implanted H ions. For olivine, the H ions implanted along the [100] direction tend to accumulate more densely at the radiation-damaged surface, while that along the [010] direction can penetrate deeper regions. In addition, increasing the temperature of H ions radiation environment enhances the capacity of the mineral to retain hydrogen. Our research provides insights for investigators aiming to comprehend the behavior of H and other H-bearing species in minerals affected by the solar wind.